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TECHNOLOGY OF COMPOSITES BASED ON KUL'-YURT-TAU PYROPHYLLITES

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The basic technical characteristics of composites based on pyrophyllite and raw rocks from the Kul'-Yurt-Tau deposit and using phosphate binders are determined. While these materials have satisfactory strength their thermal expansion and thermal conductivity are low while the frost resistance and thermal stability are high. Such materials can be recommended as refractories and building materials for use at temperatures to 1250 – 1350°C depending on the composition of the initial batch. The technology for obtaining these materials is described. Parts and refractory mixes have found applications at certain enterprises.

Key words: composite, pyrophyllite, phosphate binder, production technology, technical properties, applications experience.

An analysis of published data and research [1 – 3] has shown that in a number of cases it is best to use pyrophyllite rock as an initial material in the production of ceramic materials for fabricating parts for different applications. In the process, the possibilities of rocks from the Kul'-Yurt-Tau (Bashkortostan) and Ovruchskoe (Ukraine) deposits were compared. The general technology for obtaining parts included the following operations: preparation of the initial material, preparing batch and batching, preparation of molding mix, parts molding, drying and heat-treatment of parts and sorting and warehousing finished products.

The objective of the present work was to optimize the technology for obtaining composites based on pyrophyllite raw material and phosphate binders as well as to determine the basic technical characteristics of the materials obtained with respect to their applications in actual production.

Preparation of initial materials. Portions of samples were obtained from deposits of quartz-pyrophyllite rocks from the Kul'-Yurt-Tau deposit (QPPS) without the bulk component from different sections distributed over height and areas, taking account of pieces with the required size and color.

The rock delivered in the form of rubble was crushed in two stages: primary crushing to about 50 mm size in a SM-166 jaw crusher from the Vyksunskii plant followed by secondary crushing in a jaw crusher (Modis NOT, JSC, in Rybinsk); this gave 0.5 – 3.0 mm particles.

Fine comminution was done by the wet method in a TMNP-10/1 ball mill with uralite balls in the ratios rock : balls : water = 1 : 2 : 1. The milling was done in 48 h; the state of the water suspension was examined periodically and its fractionated composition was determined following GOST 21216.2–93.

The sour-cream-like paste obtained after wet-milling was dried in the following regime: temperature rise to 105°C — 2 h, soaking at 105°C — 4 h; temperature rise to 300 – 350°C — 1 h, soaking at 300 – 350°C — 5 h. Next, the material was comminuted by the dry method in a ball mill for 1 h to particles with specific surface area 4000 – 5000 cm^2/g with bulk mass 0.7 – 0.75 g/cm^3. The heat-resistance of this powder is at least 1540°C.

Pyrophyllite from the Ovruchskoe deposit (PP) was used in the form of a fine powder prepared by the supplier to an appropriate standard; its specific surface area was 4000 cm^2/g.

A granular fill was obtained from the pyrophyllite raw material, prepared in the manner describe above, by heat-treatment at 1200°C. After calcination the fill was crushed in a jaw crusher or similar apparatus, passed through a magnetic separator and separated into fractions by means of sieves. The powders obtained with different granular composition (coarse — 1 – 5 mm, medium — 0.1 – 1 mm, fine — 0.05 – 0.1 mm) were used to produce materials and parts.

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Technological experiments. A preliminary study of the effect of the production conditions for composites on latter's characteristics was performed on samples obtained by pressing or plastic molding. In the main, the porosity, density and compression strength of the samples, heat-treated at temperatures to 1300 – 1450°C, in the heated state as well as after cooling were measured. The pre-test cooling was performed under conditions that eliminate rehydration, which in the opposite situation leads to strength degradation. The heat-treatment regime for the samples was chosen on the basis of previous data [3]: the optimal rate of heating is 0.5 – 2 K/min below and 2 – 10 K/min above 300°C.

A strong structure in systems based on pyrophyllite raw material obtains as a result of the interaction between the phosphate binder and the filler with the formation mainly of silicon phosphates, which remain water soluble up to treatment temperatures 400°C [2]. As a result the composition is unstable; it softens, absorbing moisture from the air. At temperature close to 600°C a part of the phosphates has a crystalline and a part has an amorphous structure. Subsequent increase of the temperature eliminates the presence of water-soluble phosphates in the composition, and processes leading to the formation of other phosphates determining the strength of materials and parts are activated.

As the preliminary treatment temperature increases above 600°C the strength of all compositions increases and their properties depend more strongly on the form of the phosphate binder, the pressing pressure of the intermediate product and the treatment temperature. On the basis of consumer requirements the properties were determined in the temperature range to 1250 – 1350°C.

In the first heat treatment the composition shrinks by a small amount, 1.0 – 1.5%. The additional shrinkage occurring with subsequent heating to 1200°C is practically unobserved.

A study of the effect of the pressing pressure showed that satisfactory results are attained at 20 MPa; the strength of the composition is about 50 MPa. As the pressure increases the strength increases to 100 MPa, while the porosity decreases to 14% and depends little on the kind of binder.

The strength of the composite also increases with increasing temperature of preliminary heating irrespective of the kind of binder, reaching its maximum value (80 – 90 MPa) with 20 – 30% content of the fine fraction of the pyrophyllite raw material. Some change occurs in the density of the composites in the temperature interval 1100 – 1300°C, since on heating open pores are formed and closed pores decrease in number as a result of physical-chemical processes in the raw material and binder. The increase in the porosity and decrease in the density in this temperature interval result in some shrinkage of the composition as a result of physical-chemical processes in the binder as well as to the formation of a framework structure from the granular filler.

The investigations showed that in terms of strength, porosity and shrinkage the optimal composites have the following composition (wt.%): coarse fill 34 – 36%, medium fraction 28 – 32%, fine fraction 22 – 30% and phosphate binder 5 – 15%. It is best to use as the granular fill coarse 1 – 3, medium 0.3 – 1 and fine 0.06 – 0.16 mm particle sizes.

TABLE 1. Basic Technical Characteristics of Composites

Properties	PP-OPA	QPPS-OPA	QPPS-ACPB	PP-EC-OPA
Apparent density, g/cm^3	–	2.23	2.34	–
Open porosity, %	7.3	21.2	20.02	8.4
Ultimate compression strength, MPa	185	120	160	90
Ultimate bending strength, MPa	40 – 50	20 – 30	20 – 25	8 – 10
CLTE, 10^{-6} (20 – 1000°C)	6.6	4.1	4.6	6.4
Application temperature, °C	1300	1250	1250	1350
Thermal conductivity, W/(m · K)	0.58	0.61	0.72	0.41
Deformation onset temperature under load 0.2 MPa, °C	1320	1310	1300	1430
Heat-resistance, air heat-exchanges, more than	100	50	50	100
Frost resistance, cycle, not less than	40	50	50	60
Linear shrinkage, %	0.3	0.1	0.1	0.05

Notations: PP) pyrophyllite; QPPS) quartz-pyrophyllite schists; EC) electro-corundum; OPA) orthophosphoric acid; ACPB) aluminum-chromium-phosphate binder.

The heat resistance determined for samples based on pyrophyllite and mixed (in a mixture with corundum) fillers exceeded 100 heat cycles (1000°C – water). The deformation onset temperature under a 0.2 MPa load lies above 1300°C, and it is somewhat lower for compositions based on OPA than ACFB. The linear thermal expansion coefficient of the experimental compositions was less than that of compositions based on corundum, which gives them a comparatively high heat-resistance.

The results obtained were used as a basis to develop composites with two compositions based on granular fill made from calcined pyrophyllite raw material; their main characteristics are presented in Table 1.

Production technology. The technological process used to produce ceramic parts based on pyrophyllite raw material and phosphate binders can be represented in the general case by the diagram displayed in Fig. 1. For each actual manufactured part it can be somewhat different, but the main stages remain: the preparation of the molding mix, molding, drying and heat-treatment of blanks. In some cases the kilned parts can undergo additional mechanical working.

Molding mix preparation. Different types of mixers were used depending on the form of the molding mix and the subsequent method of molding: blade mixer — for preparing semidry mixes; concrete mixers — for liquid mixers; extruder — for plastic mixes.

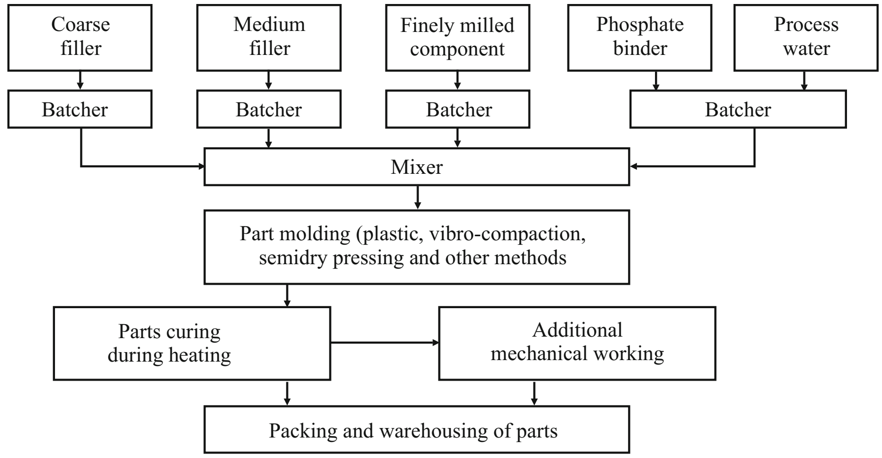

Fig. 1. Technological scheme of the production ceramic composites based on pyrophyllite and phosphate binder.

Parts molding. Semidry pressing was used to obtain dense parts with the minimum content of the phosphate binder. Vibro-compaction together with mobile mixes was used for parts with a complex shape and moderate density. Plastic molding with an extruder was used to fabricate ceramic tubes for electric insulation applications.

Heat-treatment of parts. The heat-treatment of parts is an important and in many cases the final production stage, since water is removed, gases are released, polymorphic transformations occur in the material, the dimensions and density of the parts change and new crystalline and amorphous phases are formed.

Batch action or continuous action drying units were used to remove moisture to residual content 0.2 – 2.0%. The former are used mainly for large parts; the latter (conveyer, tunnel) have a larger capacity and are usually used for medium- and small-size parts.

The subsequent heat-treatment and cooling were conducted in a prescribed temperature regime taking account of the dimensions of the parts and the furnace design. For this, batch action electric resistance furnaces with silit and other heaters were used.

A technology of composites based on pyrophyllite raw materials from the Kul’-Yurt-Tau deposit and a process line for part production were developed at the final stage of the research.

Applications experience. This work resulted in the fabrication of refractory pastes, electric insulation parts and lining elements for the thermal units used in the production of construction materials. Specifically, the lining elements (Fig. 2) of the Aichelin quench units, which are used at the enterprise Belebey Plant Avtonormal’, JSC, were made using the new refractory paste. Parts with the prescribed shape have a uniform low-shrinkage structure; their compression strength is several-fold greater than that of parts made from fireclay.

Plastic molding was used to fabricate two kinds of electric insulation parts — bushings and tubes with different di-

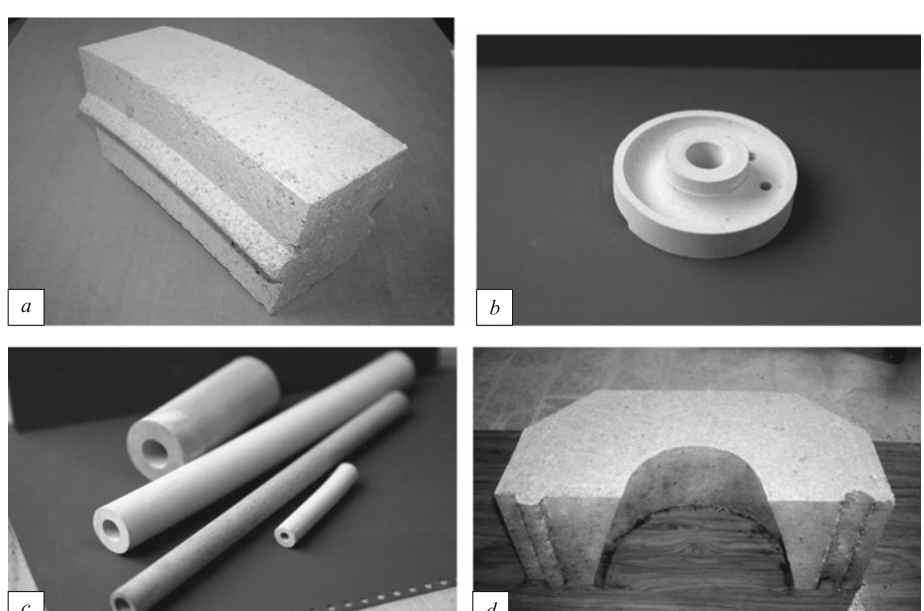

Fig. 2. Form of parts made from composite materials.

ameters for Dimitrovgrad Auto Aggregate Plant and heating units (insulation for current lead-ins).

Technical Characteristics of Parts Fabricated by Plastic Molding

Ultimate compression strength, MPa	≥ 50
Additional linear shrinkage at 1200°C, %	≤ 0.5
Thermal stability (800°C – water), cycles	50
Operating temperature, °C	1300

Burner blocks for Ipsen quench furnaces, used at the enterprise Belebey Plant Avtonormal', JSC, were fabricated using refractory mixes with coarse-grain filler. The parts with the prescribed shape had a uniform structure (see Fig. 2).

Technical Characteristics of Parts Fabricated from Refractory Mixes with Coarse-Grain Filler

Ultimate compression strength, MPa	≥ 80
Open porosity, %	18.5
Apparent density, g/cm^3	2.47
Linear shrinkage (growth) at 1300°C, %	0 – 0.1
Thermal stability, cycles, %	≥ 10

CONCLUSIONS

The addition of pyrophyllite raw material to compositions with granular fillers based on phosphate binders lowered the curing temperature of materials (to room temperature for aluminum-chromium-phosphate binder), increased the strength at moderate temperatures (to 700°C), significantly reduced the degree of softening in the interval 700 – 1000°C and increased the thermal stability. With heat-treatment above 1200°C a small amount of a liquid phase (silicon pyrophosphate) is formed in the material. The amount of this phase decreases with decreasing pyrophyllite content.

The technology producing pyrophyllite-phosphate materials has specific features due to acid-base interaction processes and structure formation and hardening. The technology is distinguished by simplicity and does not require large energy and capital inputs, since heat-treatment is done, as a rule, at temperatures no higher than 700°C; heat-treatment at higher temperature is used only in certain cases. Examples of the fabrication of parts which have found applications in production were presented.

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